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## Aqueous Behavior of Aluminum Oxychloride

2 MARCH 1964

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Aerodynamics and Propulsion Research Laboratory*

*Prepared for COMMANDER SPACE SYSTEMS DIVISION*

UNITED STATES AIR FORCE

*Inglewood, California*

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This technical documentary report has been reviewed and is approved for publication and dissemination. The conclusions and findings contained herein do not necessarily represent an official Air Force position.

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## ABSTRACT

Contrary to a previous report, anhydrous AlOCl dissolves readily in water to form a solution that is stable toward hydrolysis, even at 100°C. Concentrated solutions disproportionate appreciably to aluminum trichloride and aluminum oxide at 100°, but not at 60°C. The strong conductance of aqueous AlOCl solutions, combined with freezing point depression data, indicate that dissolved AlOCl is polymerized. A crystalline hydrate AlOCl· 2.5H<sub>2</sub>O has been isolated. Pyrolysis of this hydrate at 100°C leads to the formation of a lower hydrate, approaching the composition AlOCl· H<sub>2</sub>O. At temperatures of 200-300°C, pyrolysis of the hydrate leads to an almost anhydrous AlOCl. However, these pyrolytic dehydration reactions are accompanied by a competing reaction which evolves HCl and forms AlO(OH). The latter compound can be kept to a minimum by carrying out the pyrolysis at higher temperatures where dehydration requires shorter reaction times; our data indicate that the dehydration reaction is more temperature dependent than is the reaction forming AlO(OH) + HCl.

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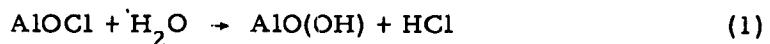
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## I. INTRODUCTION

Because aluminized solid propellants currently in use employ an oxidizer containing both oxygen and chlorine, it is possible that crystalline aluminum oxychloride is an exhaust species. At present, sufficient thermodynamic data for the evaluation of AlOCl(s) as an exhaust product are not available. The only species considered is gaseous AlOCl. One of the objectives of our program is the attainment of thermodynamic data on AlOCl(s). For this reason a knowledge of the aqueous reactions of AlOCl is of importance in planning thermochemical studies. Since there is also an interest in preparing AlOF(s) for examination as a possible high energy exhaust species, the authors have investigated the aqueous chemistry of AlOCl as a possible means of preparing crystalline AlOF.

Although anhydrous aluminum oxychloride has been prepared by a variety of reactions,<sup>1,2</sup> there is scant information about its solution properties. It has been reported to be insoluble in organic solvents, and to react readily with water, hydrolyzing rapidly at room temperature according to Eq. (1).<sup>2</sup>



Contrary to Rouxel's report,<sup>2</sup> we have found that AlOCl forms stable aqueous solutions without hydrolysis, even at 100°C. Details of the aqueous behavior of AlOCl and the formation of crystalline hydrates follow.

## II. EXPERIMENTAL

### A. PREPARATION OF AlOCl

Anhydrous AlOCl was prepared by the reaction of  $\text{AlCl}_3$  and  $\text{As}_2\text{O}_3$  to form AlOCl and  $\text{AsCl}_3$ ; <sup>1</sup> an exception was the use of a stainless steel bomb to carry out the reaction at  $240^\circ\text{C}$ . Excess  $\text{AlCl}_3$  and the byproduct  $\text{AsCl}_3$  were removed from the AlOCl by high vacuum distillation. A small non-volatile impurity remained, but this impurity was insoluble in water and could be easily separated from AlOCl. The chlorine content of the latter was verified by precipitation of  $\text{AgCl}$  from acidic solution.

### B. AQUEOUS SOLUTIONS OF AlOCl

Anhydrous AlOCl dissolved readily in water without evidence of hydrolysis, according to Eq. (1); there was no HCl evolution or formation of an insoluble hydroxide. Heating dilute solutions at  $100^\circ\text{C}$  for 1 to 2 hours also produced no evidence of hydrolysis. Freezing point depressions were taken on 0.21 and 0.22 molar solutions. From these data an average apparent molecular weight of 76.5 was obtained; the theoretical formula weight of AlOCl is 78.5. The conductances of 0.1 molar solutions of AlOCl were compared to solutions of KCl and acetic acid of the same molarity. At an applied voltage of 9 V, the ratios of currents for KCl/AlOCl and AlOCl/HAc were 3.1 and 6.5.

A dilute aqueous solution of AlOCl was evaporated by boiling at atmospheric pressure and  $100^\circ\text{C}$ . The evaporation was continued until the solution became very concentrated and separation of a precipitate was noted; HCl was not evolved. Further removal of the solvent was carried out under high vacuum at a temperature of about  $60^\circ\text{C}$ ; the residue was further evacuated at room temperature for several days. Although the residue was shown by elemental analysis to have an overall composition of  $\text{AlOCl} \cdot 3\text{H}_2\text{O}$ , x-ray diffraction examination showed the presence of a considerable quantity of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .

Although aqueous solutions of AlOCl alone do not hydrolyze, they are hydrolyzed by base. Addition of excess NaOH to a 0.21 molar solution of AlOCl at room temperature resulted in a quantitative precipitation of aluminum hydroxide.

C.  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$

The aqueous solvent was distilled from a solution of AlOCl under high vacuum, at temperatures of about  $60^{\circ}\text{C}$ . A solid residue was formed. Prolonged evacuation of the latter at room temperature under high vacuum until constant weight was obtained resulted in the isolation of  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$ . An attempt was made to obtain the x-ray diffraction spectrum of this hydrate but was unsuccessful because of its small particle size. However, it was shown by its electron diffraction pattern that the hydrate is crystalline. The diffraction spectrum is given in Table 1.

Table 1. Comparison of Diffraction Patterns of  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$  and AlOCl

Electron Diffraction Spectrum of $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$	X-Ray Diffraction Spectrum of $\text{AlOCl}^2$	
Interplanar Spacings, $\text{\AA}^*$	Interplanar Spacings, $\text{\AA}^*$ , Intensity	
4.26	-	
3.76	-	
3.25	3.35	100
2.96	2.75	46
2.54	2.46	23
2.32	2.29	1
2.24	2.19	2
1.91	1.94	6
1.63	1.64	2
1.52	1.52	3

\*These electron diffraction data are accurate to about  $0.2 \text{\AA}$  at interplanar spacings of  $4 \text{\AA}$ , and  $0.1 \text{\AA}$  at spacings of  $2 \text{\AA}$ .

It was found that the hydrate is readily soluble in water, giving a freezing point depression that yields an apparent molecular weight which is only slightly higher than the formula weight for  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$ .

#### D. PYROLYSIS OF $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$

A preparation consisting of 0.00475 mole of  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$  was heated for 3 hours with a  $100^\circ\text{C}$  bath in a high vacuum system containing a trap at  $-195^\circ\text{C}$ . At that time the contents of the residue and the condensed species in the trap were analyzed. The residue was then heated similarly for an additional 3 hours and the newly evolved material and residue were analyzed. It was found that 89.2 percent of the evolved gas was driven off during the first 3 hours of pyrolysis and only 10.8 percent during the second 3 hours. The gas driven off during the entire 6 hour pyrolysis consisted of 0.00068 mole HCl and 0.00603 mole  $\text{H}_2\text{O}$ . The residue consisted of 0.00407 mole  $\text{AlOCl}$ , 0.00068 mole  $\text{AlO(OH)}$ , and 0.00517 mole of water. If the water were associated only with  $\text{AlOCl}$ , the aluminum oxychloride hydrate at this point would be  $\text{AlOCl} \cdot 1.27\text{H}_2\text{O}$ ; if the water were associated equally with the  $\text{AlO(OH)}$ , then the composition would be  $\text{AlOCl} \cdot 1.09\text{H}_2\text{O}$ . After 6 hours of pyrolysis at  $100^\circ\text{C}$ , 14.3 percent of the original  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$  had decomposed to produce  $\text{AlO(OH)} + \text{HCl}$ .

The hydrate resulting from the 6 hours of pyrolysis at  $100^\circ\text{C}$  was then heated in a bath at  $200^\circ\text{C}$  for 3 hours (plus about 1 hour while the bath was attaining temperature) in the same high vacuum apparatus. During this time 0.00125 mole HCl and 0.00328 mole  $\text{H}_2\text{O}$  were evolved, and the residue consisted of 0.00282 mole  $\text{AlOCl}$ , 0.00193 mole  $\text{AlO(OH)}$  and 0.00064 mole  $\text{H}_2\text{O}$ . This is consistent with a residue composition containing  $\text{AlOCl} \cdot 0.23\text{H}_2\text{O}$ , if all the water is associated with  $\text{AlOCl}$ , and  $\text{AlOCl} \cdot 0.13\text{H}_2\text{O}$ , if the water is also associated with  $\text{AlO(OH)}$ . Considering the combined pyrolyses at 100 and  $200^\circ\text{C}$ , the total decomposition of the original hydrate to produce  $\text{AlO(OH)} + \text{HCl}$  was 40.6 percent.

Another  $\text{AlOCl}$  hydrate, of composition  $\text{AlOCl} \cdot 4.5\text{H}_2\text{O}$ , was pyrolyzed at about  $300^\circ\text{C}$  (by a heating mantle) for 2 hours. In this case 0.000815 mole of hydrate gave a residue of 0.000673 mole  $\text{AlOCl}$ , 0.00011 mole water, and 0.000142 mole  $\text{AlO(OH)}$ . This corresponds to a final aluminum oxychloride residue consistent with  $\text{AlOCl} \cdot 0.16\text{H}_2\text{O}$ , if all the water were associated with the  $\text{AlOCl}$ , and  $\text{AlOCl} \cdot 0.135\text{H}_2\text{O}$ , if the water were also associated with  $\text{AlO(OH)}$ . In this case the decomposition of the original hydrate to produce  $\text{AlO(OH)} + \text{HCl}$  was 17.4 percent, considerably less than in the previous experiments at lower temperatures, despite the fact that dehydration was even more complete at  $300^\circ\text{C}$ .

A final residue from pyrolysis of the hydrated  $\text{AlOCl}$ , of very low water content, was extracted with 40 cc of diethyl ether. This extract was then distilled, leaving no residue. This absence of  $\text{AlCl}_3$  verifies that disproportionation does not occur during pyrolysis of the crystalline hydrate. That the final residue, which is a mixture of  $\text{AlOCl} \cdot 0.1\text{H}_2\text{O}$  and  $\text{AlO(OH)}$ , contains a water-soluble component in addition to the insoluble hydroxide was verified during the final chlorine assay. Addition of aqueous  $\text{AgNO}_3$  to the aqueous extract of the final residue gave an instantaneous precipitate of  $\text{AgCl}$ ; the insoluble hydroxide was then dissolved in excess nitric acid.

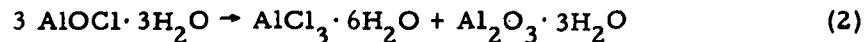
X-ray diffraction spectra of the final dehydrated residue [ $\text{AlOCl} + \text{AlO(OH)}$ ] were taken, but they gave no discernible patterns. The electron diffraction spectrum was incomplete, but it gave within experimental error the major 2.32, 2.13 and 1.63 Å lines of  $\text{AlO(OH)}$ , along with minor lines at 1.26, 1.18 and 1.09 Å.

### III. CONCLUSIONS

It is evident that aqueous solutions of  $\text{AlOCl}$  are quite stable at ordinary temperatures and that hydrolysis, if it occurs at all, is exceedingly slow.

Because dissociation of AlOCl in water to the simple species  $\text{AlO}^+$  (or hydrated ions of  $\text{AlO}^+$ ) and  $\text{Cl}^-$  would result in an appreciable rate of hydrolysis, such cations do not exist in the solution. This is verified by the freezing point depression data which indicate an apparent molecular weight equivalent to the formula weight. However, it is also clear that monomeric AlOCl does not exist as such to any appreciable extent because of the reasonably strong electrolyte behavior of the solution; the conductance of the latter is much greater than that of the weak electrolyte acetic acid and approaches that of the strong electrolyte, KCl. The identity of the dissolved species is undoubtedly complex, with the data indicating that AlOCl polymerizes prior to dissociation. In view of the tendency of aluminum to attain a higher coordination number than would be characteristic of the formulation AlOCl, it is probable that the polymerized species in solution strive to attain a coordination number of 6 for aluminum, possibly augmented by water of hydration.

While aqueous solutions do not hydrolyze appreciably, even at  $100^\circ\text{C}$ , the large-scale formation of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  when concentrated solutions of AlOCl are heated at  $100^\circ$  indicates that disproportionation occurs under such conditions, with conversion of aluminum oxychloride to aluminum trichloride and aluminum oxide. Material balance is shown by Eq. (2) for the trihydrate formed in this particular experiment.



Because a bath of  $60^\circ\text{C}$  was used for the distillation of the solvent in the isolation of  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$  and the diffraction pattern for  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  was entirely absent from the diffraction pattern of this hydrate (see Table 1), it is evident that disproportionation does not occur to any appreciable extent at  $60^\circ\text{C}$ . This is also verified by the freezing point data and by the absence of  $\text{AlCl}_3$  in the dehydrated residue or the material evolved from the hydrate upon pyrolysis. Disproportionation in solution thus requires strong reaction conditions.

The crystalline hydrate  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$  readily forms the initial aqueous solution upon re-solution in water, as demonstrated by the freezing point depression data. Its overall composition of  $\text{AlOCl} \cdot 2.5\text{H}_2\text{O}$  is quite similar to a hydrate reported by Kohlschütter and co-workers<sup>3</sup> who isolated a compound given as  $\text{AlOCl} \cdot 2.7\text{-}3.0\text{H}_2\text{O}$  from an aqueous solution of the so-called "2/3 basic aluminum chloride." This solution was formally described as aqueous  $\text{Al(OH)}_2\text{Cl}$ , but it was shown that this species could not exist as such in the solution. From their freezing point data and conductivity data, it appears that the "2/3 basic aluminum chloride" solution, prepared from  $\text{Al} + \text{HCl}$  in aqueous medium, is identical to that formed by the solution of anhydrous  $\text{AlOCl}$  in water. We repeated their experiment, isolating a hydrate corresponding to  $\text{AlOCl} \cdot 2.78\text{H}_2\text{O}$ , but the latter was not sufficiently crystalline for comparison with the data in Table 1.

Our efforts to recover anhydrous  $\text{AlOCl}$  from its aqueous solution were only partially successful. Prolonged evacuation under high vacuum at temperatures not above  $60^\circ\text{C}$  leads to a crystalline hydrate rather than to the anhydrous  $\text{AlOCl}$ . Pyrolysis of this hydrate at  $100^\circ\text{C}$  does drive off further water, but the product is a lower hydrate (approximately  $\text{AlOCl} \cdot \text{H}_2\text{O}$ ) rather than  $\text{AlOCl}$  itself. Further, at this temperature a competing reaction occurs, involving  $\text{HCl}$  evolution and the formation of  $\text{AlO(OH)}$ . It is interesting that this reaction, which is formally analogous to the hydrolysis reaction of Eq. (1), proceeds upon pyrolysis of the crystalline hydrate at a temperature where the aqueous solution does not hydrolyze appreciably.

More complete dehydration than that obtainable at  $100^\circ\text{C}$  is achieved by pyrolysis of the hydrate at  $200$  or  $300^\circ\text{C}$ . From the data at  $100$ ,  $200$  and  $300^\circ\text{C}$ , it is clear that the dehydration reaction is more temperature dependent than the decomposition reaction leading to  $\text{AlO(OH)} + \text{HCl}$ . Considerably less  $\text{AlO(OH)}$  is formed at  $300^\circ\text{C}$  where almost complete dehydration can be achieved in about 2 hours than at  $200^\circ\text{C}$  where longer reaction times are required for a comparable degree of dehydration.

Whereas disproportionation occurs in concentrated aqueous solutions at 100°C, it is absent in the pyrolysis of the crystalline hydrate, even at temperatures as high as 300°C. Disproportionation occurs upon pyrolysis of anhydrous AlOCl at much higher temperatures.<sup>4,5</sup>

From a comparison of the data in Table 1, it can be seen that most of the interplanar spacings for the crystalline hydrate correspond to analogous spacings in the structure of anhydrous AlOCl; the discrepancies are well within experimental error for the less exact measurements possible by electron diffraction. The lines at 4.26 and 3.76 Å are not in anhydrous AlOCl. Because they are the strongest of the observed lines, they are evidently associated with the aqueous linkage rather than with AlO or AlCl. The only major line present in AlOCl and not in the crystalline hydrate is the 010 line at 8.23 Å.

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